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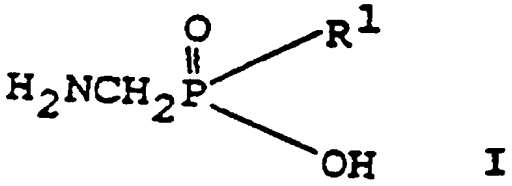
(54) Titre : METHODE DE PREPARATION D'ACIDE AMINOMETHANEPHOSPHONIQUE ET D'ACIDES AMINOMETHYLPHOSPHINIQUES

(54) Title: PROCESS FOR THE PREPARATION OF AMINOMETHANEPHOSPHONIC ACID AND AMINOMETHYLPHOSPHINIC ACIDS



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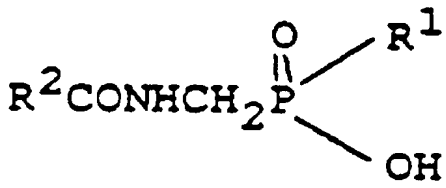


II

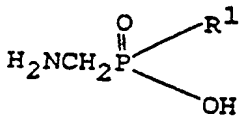
(57) Abrégé/Abstract:
Aminomethanephosphonic acid and aminomethylphosphinic acids are interesting as biologically active compounds or as intermediates for the preparation of biologically active compounds. According to the invention, such compounds of the formula I (see formula I) in which R^1 is OH, C_1-C_4-alkyl or phenyl, can be prepared in a techincally simple manner by reacting compounds of formula II (see formula II) in which R^2 is H, C_1-C_6-alkyl, benzyl, phenyl, optionally substituted by C_1-C_4-alkyl, -alkoxy and/or halogen, and R^1 is defined above, with water, at 80 to 300°C.

HOE 90/F 249

Abstract of the disclosure:

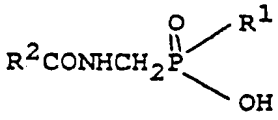
Process for the preparation of aminomethanephosphonic acid and aminomethylphosphinic acids

Aminomethanephosphonic acid and aminomethylphosphinic acids are interesting as biologically active compounds or as intermediates for the preparation of biologically active compounds. According to the invention, such compounds of the formula I



I

in which R^1 is OH, C_1-C_4-alkyl or phenyl, can be prepared in a technically simple manner by reacting compounds of the formula II



II

in which R^2 is H, C_1-C_6-alkyl, benzyl, phenyl, optionally substituted by C_1-C_4-alkyl, -alkoxy and/or halogen, and R^1 is as defined above, with water, at 80 to 300°C.

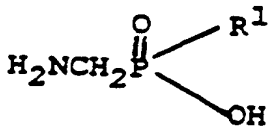
Description

Process for the preparation of aminomethanephosphonic acid and aminomethylphosphinic acids

Herbicidal and plant-growth-regulating actions are known of aminomethanephosphonic acid; aminomethylphosphinic acids are also industrially valuable compounds having a biological activity or can be used as intermediates for the preparation of biologically active compounds (see the article by L. Maier "Advances in the Chemistry of Aminophosphinic Acids" in the periodical "Phosphorus and Sulfur" 1983, Vol. 14, p. 295-322, in particular 317-323 and literature cited therein). Aminomethanephosphonic acid is furthermore valuable as an intermediate for the preparation of N-phosphonomethylglycine (see EP-A-214,578).

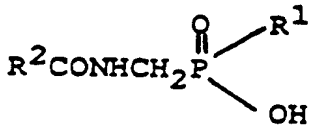
Aminomethanephosphonic acid can be prepared from acylaminomethanephosphonic acids by hydrolysis with hydrochloric acid (US-A-2,304,156; US-A-2,328,358; M. Soroka, Synthesis 1989, 547). It is a disadvantage of this process that the aminomethanephosphonic acid can only be obtained in high yields during working-up when special measures are applied. For example, M. Soroka describes working-up with the aid of pyridine or propylene oxide, which cause the separation of hydrogen chloride from the aminomethanephosphonic acid. Another disadvantage is that, without complicated ultrapurification, the acylaminomethanephosphonic acids contain traces of formaldehyde, due to the production process. The treatment with hydrochloric acid in the hydrolysis then results in the formation of bischloromethyl ether as undesirable by-product, which has been identified clearly as a carcinogenic working substance. There is therefore a demand for hydrolysis processes which can be carried out on an industrial scale and which exclude the formation of the by-product bischloromethyl ether.

The invention relates to a process for the preparation of compounds of the formula I



I

in which R^1 is hydroxyl, C_1-C_4-alkyl, preferably C_1-C_2-alkyl, in particular methyl, or is phenyl, which comprises reacting acylaminomethanephosphonic or acylaminomethylphosphinic acids of the formula II



II

in which R^2 is hydrogen, alkyl having 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms, or is benzyl or phenyl, unsubstituted or substituted by one or more radicals from the group comprising C_1-C_4-alkyl, C_1-C_4-alkoxy and halogen, and R^1 is as defined above, with water, at 80 to 300°C, preferably 150 to 250°C.

Some of the starting substances of the formula II are known, or some are accessible analogously to known methods. For example, the acylaminomethanephosphonic acids of the formula II can be prepared from N-(hydroxymethyl)amides and PCl_3 (see US-A-2,328,358; US-A-2,304,156 or M. Soroka, Synthesis 1989, 547 and literature cited therein).

The acylaminomethanephosphonic acids as well as the acylaminomethylphosphinic acids of the formula II can also be prepared by the process in German Patent Application P 4,026,026.7.

Examples of preferred starting substances of the

formula II are formylaminom thanephosphonic acid, acetylaminomethanephosphonic acid, benzoylaminomethan - phosphonic acid, (acetylaminomethyl)(methyl)phosphinic acid and (benzoylaminomethyl)(phenyl)phosphinic acid.

The starting substances of the formula II are treated with water, if appropriate with an excess of water, and the mixture is brought to reaction temperature, and it may be necessary to carry out this process under pressure, as a function of the temperature.

The extent of the excess of water is not particularly critical for the reaction; for example, for reasons of better handling, it may be advantageous to use a 2 to 30 molar, preferably 10 to 25 molar, excess of water. The reaction temperatures are 80 to 300°C, preferably 150 to 250°C. The reaction times depend on the substrate, reaction temperature and pressure and are generally in the range from 5 to 40 hours, preferably 10 to 35 hours.

When the reaction is complete, working-up can be carried out in a simple manner, for example by removing the carboxylic acid as a solid (for example benzoic acid) or by distillation (for example acetic acid). The resulting aminomethanephosphonic acid, or aminomethylphosphinic acids, generally already have high purity. If appropriate, they can be obtained in ultrapure form by customary methods, preferably by crystallization.

Example 1

20 g (0.093 mol) of benzoylaminomethanephosphonic acid and 20 g of water were placed in a sealed tube and maintained at 200°C for 20 hours. After cooling, the reaction material was digested with 100 ml of water. The benzoic acid was subsequently filt red off with suction. The filtrat was conc ntrated in vacuo by distillation until it had reached an internal temperature of 75°C. There remained 10.3 g (100 % of th ory) of aminomethan -

phosphonic acid which, according to ^{31}P-NMR spectrum analysis, had a purity of 95 %.

Example 2

20 g (0.093 mol) of benzoylaminomethanephosphonic acid and 20 g of water were placed in a sealed tube and maintained at 150°C for 20 hours. After cooling, the reaction material was then digested with methanol and filtered off with suction. 8.2 g (80 % of theory) of aminomethanephosphonic acid of a decomposition point of 310°C were obtained.

Example 3

20 g (0.093 mol) of benzoylaminomethanephosphonic acid and 20 g of water were refluxed for 30 hours. After cooling, the reaction material was digested with 100 ml of methanol and filtered off with suction. 5.3 g (52 % of theory) of aminomethylphosphonic acid of a decomposition point of 275°C were obtained. Unreacted benzoylaminomethanephosphonic acid could be isolated from the filtrate.

Example 4

21.3 g (0.1 mol) of benzoylaminomethylmethylphosphinic acid and 42 g of water were placed in a sealed tube and maintained at 200°C for 20 hours. After cooling, the mixture was digested with water, and benzoic acid was removed by filtration with suction. The filtrate was evaporated to dryness in vacuo. The crystalline residue was digested with methanol and filtered off with suction. 8 g (73 % of theory) of aminomethylmethylphosphinic acid of a melting point of 255-261°C were obtained.

Example 5

20 g (0.073 mol) of benzoylaminomethylphenylphosphinic

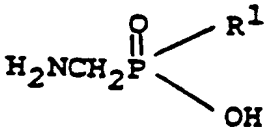
acid and 40 ml of water were placed in a sealed tube and maintained at 225°C for 23 hours. The benzoic acid was then removed by filtration with suction, followed by rinsing with water. The filtrate was concentrated to dryness in vacuo. There remained 12.5 g (100 % of theory) of crude aminomethylphenylphosphinic acid. After digestion with methanol, the substance obtained had a melting point of 276-278°C.

Example 6

14.4 g (0.094 mol) of acetylaminomethanephosphonic acid and 28 g of water were fed into a sealed tube and maintained at 200°C for 20 hours. The mixture was then cooled, and the resulting reaction solution was freed in vacuo from water and acetic acid. The residue was digested with a mixture of 30 ml of methanol and 1 ml of water. 9.6 g (92 % of theory) of aminomethanephosphonic acid of a decomposition point of 270-278°C were obtained.

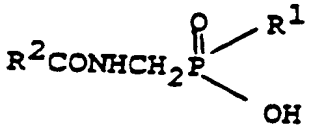
Patent claims:

1. A process for the preparation of compounds of the formula I



I

in which R^1 is hydroxyl, C_1-C_4-alkyl or phenyl, which comprises reacting acylaminomethanephosphonic or acylaminomethylphosphinic acids of the formula II



II

in which R^2 is hydrogen, alkyl having 1 to 6 carbon atoms, benzyl or phenyl, unsubstituted or substituted by one or more radicals from the group comprising C_1-C_4-alkyl, C_1-C_4-alkoxy and halogen, and R^1 is as defined above, with water, at 80 to 300°C.

2. The process as claimed in claim 1, in which R^1 is hydroxyl.

3. The process as claimed in claim 1, in which R^1 is methyl, ethyl or phenyl.

4. The process as claimed in claim 1, 2 or 3, in which R^2 is H, C_1-C_3-alkyl, benzyl or phenyl.

5. The process as claimed in claim 1, 2 or 3, in which R^2 is phenyl.

6. The process as claimed in one or more of claims 1 to 5, in which the reaction temperature is 150 to 250°C.

7. Th process as claim d in one or more of claims 1 to 6, in which a 2 to 30 molar xc ss of wat r, based on 1 mol of compound of th formula II, is employed.

8. The process as claimed in one or more of claims 1 to 7, in which the reaction time is in the range from 5 to 40 hours.

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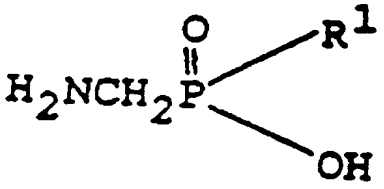

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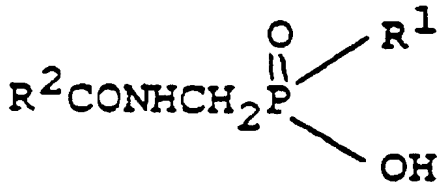

II